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STUDIES OF THE EFFECT OF LASER RADIATION ON CHEMICAL ACTIVATION AND VAPOR FOG NUCLEATION

FINAL REPORT

BY

CHARLES S. NAIMAN
IRWIN L. GOLDBLATT
JACK SCHWARTZ

MARCH 1967

PHYSICAL RESEARCH LABORATORY
RESEARCH LABORATORIES
EDGEWOOD ARSENAL, MARYLAND 21010

CONTRACT DA-18-035-AMC-255(A)

MITHRAS, INC.

AEROTHERMODYNAMICS – ELECTROMAGNETICS – QUANTUM PHYSICS

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Edgewood Arsenal, Maryland 21010
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Task 1C622401A09501

FOREWORD

The work described in this report was authorized under Project 1C622401A095, Basic Research in Life Sciences. This work was started in June, 1964 and completed in June, 1966. The experimental data are contained in MITHRAS Notebooks No. 25, 19, 7B, S-4, and S-23.

ACKNOWLEDGMENTS

We wish to acknowledge the advice of Prof. J. Ducuing formerly of Massachusetts Institute of Technology, presently at the University of Paris, who was of considerable help with the ruby laser technology. Dr. Paul Rabinowitz of Brooklyn Polytechnic Institute, also Prof. A.Javan of Massachusetts Institute of Technology, along with some of his students, contributed very practical advice on the design and operation of CO_2 laser equipment. Prof. K. Biemann and Mr. R. Hites of the Massachusetts Institute of Technology Chemistry Department provided mass spectroscopic measurements on chemical samples plus valuable advice on sample preparation and on interpretation of the spectra. The National Magnet Laboratory at the Massachusetts Institute of Technology, at which one of the authors (JS) is a guest scientist, provided us with the use of some of its facilities for NMR spin echo experiments, and for some of our CO_2 laser experiments. Professor C. Steel of the Brandeis University Chemistry Department provided the azo compounds used in some studies of laser effects.

DIGEST

This is a Final Report which reviews observations of laser effects on DMMP under various conditions, with the ultimate objective of decontamination or protection applications in which laser irradiation might be of value. Among the conclusions are:

(1) Ruby laser effects on vapor fog nucleation are not observable without extremely high intensities, and even then, physical condensation requires very carefully controlled laboratory conditions.

(2) Ruby lasers produce very little chemical decomposition, at the power levels available in this study, and require intensities at least sufficient to produce dielectric breakdown at the laser frequency.

(3) The CO_2 laser produces chemical decomposition in liquid DMMP at normal intensities. The decomposition products do not differ from simple heating effects, but are of sufficient magnitude to justify further laboratory studies.

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1.0 INTRODUCTION AND PUBLICATIONS

This is a Final Report on a two-year study of laser radiation effects. In view of the broad scope of this work, and of the considerable changes in technology that took place since its beginning, we shall quote here the objectives and the work statement with which this work was begun. This report is intended to provide perspective on the entire project. Detailed discussions and numerical values are in the progress reports and will not be duplicated here.

There are three general objectives which are itemized with Roman numerals. This report is organized so that one numbered section will be devoted to each of the numbered objectives and the corresponding Roman numeral will be identified in the title of the section. An additional section will cover general techniques used in this study which are not necessarily restricted to any one of the objectives. Final sections will deal with conclusions from this study and with recommendations for future work.

Objective

This contract will provide basic information on the effect of molecular activation caused by radiation from lasers. To be included is the study of the effects of the radiation upon the reaction rates of the activated species. Also to be investigated are the effects of radiation from lasers upon the condensation of aerosol fogs. Such basic studies will provide information for selecting and evaluating systems for protection and decontamination.

Work Statement

The work to be performed can be divided into three portions.

(I) The first portion will provide basic information on the effects caused by radiation from lasers upon the rates of decomposition of vapor systems comprised of, but not limited to, the simulant dimethyl methylphosphonate. The first portion will only be pursued if time and funds permit, and only after necessary effort has been expended on the second and third portion of work under the contract.

(II) The second portion will provide basic information on the activation of the oxygen and/or other components of the air by means of radiation from lasers. To be included is a study of the subsequent reactions of the activated species with simulants and other unactivated species present.

(III) The third portion of the work will provide basic information upon the condensation of aerosol fogs using radiation from lasers.

Inherent to each of these portions are the supplementary studies of infrared, ultraviolet, and visible spectra of the molecules; the laser technology; the effects of optical pumping; and the use of "forbidden" transitions.[11]

Itemizing our work in the reverse order is most convenient chronologically.

Publications

A number of publications have resulted from work supported by this contract. For convenience these are listed below. Copies of each talk or paper will be found in Quarterly Progress Reports under this contract, as indicated.

(1) C.S.Naiman, J. Schwartz, M.Y. DeWolf, and I.L. Goldblatt, Paper No. 7A-6, Quantum Electronics Conference at Phoenix, Arizona, April 1966 (unpublished), "Laser Induced Breakdown and Pre-breakdown Phenomena Observed in Cloud Chambers." (A copy is provided in QPR No. 7, Appendix C.)

(2) C.S.Naiman, M.Y. DeWolf, I. L. Goldblatt, and J. Schwartz, Phys. Rev. 146, 133 (1966). (A copy is provided in QPR No. 5, Appendix A.)

(3) M.Y. DeWolf, "The NMR Spectra of Dimethyl Methyl Phosphonate," J. Molecular Spectroscopy, 18, 59 (1965). (Also discussed in QPR No. 2, Section 2.1 and in QPR No. 4, Section 2.1).

(4) C.S.Naiman, M.Y.DeWolf, J. Schwartz, Bull. Am. Phys. Soc., Ser. II, 10 (1965), "A Study of Nucleation Induced by Laser Irradiation." (Also discussed in QPR No. 2, Section 2.4; QPR No. 3, Section 2.4; and QPR No. 4, Section 2.4.)

(5) M.Y. DeWolf, "NMR Study of Dimethyl Methylphosphonate," Bull. Am. Phys. Soc., Ser.II, 10 (1965). (Also discussed in QPR No. 1; QPR No. 2, Section 2.1; and QPR No. 4, Section 2.1.)

2.0 CONDENSATION OF AEROSOL FOGS (Item III)

We have observed the physical reaction of aerosol fogs to ruby laser irradiation over a considerable range of conditions. The cloud chamber was a convenient laboratory tool for many of these investigations, as it readily provided a (highly polydisperse) aerosol fog. Our observations can be extrapolated to conditions more likely to be encountered in practice.

2.1 Observations in Transparent Media (Non-Resonant Laser Effects)

With exclusively transparent media under ruby laser irradiation, the following observations were made on the condensation of supersaturated vapors as a function of optical electric field strengths attained by laser action. Where no effects were observed with supersaturated vapors, even less is to be expected at lower concentration levels of DMMP by way of physical effects. (Other chemical means of agglomeration are the subject of Item II of our work statement.)

At electric field levels high enough to cause air breakdown in an ordinary atmosphere*, supersaturated DMMP vapors will condense to form a highly polydisperse aerosol fog.[1] Exposure of this fog to further irradiation does not lead to droplet growth, nor disperse the aerosol, except perhaps for highly localized effects which might have escaped observation in the highly turbulent conditions prevalent in the aerosol fog.

In a very narrow range of intensities just below breakdown levels (10^7 to 10^8 volts/cm), where we observed "pre-breakdown ionization," large agglomerations of droplets were found at the focal point, which rapidly dropped to the bottom of the chamber. (These effects were not photographable, but are described in our publications[2, 3]; also in Quarterly Progress Report No. 4, page 9 and Quarterly Progress Report No. 5, Appendix A.)

Below these intensity levels, there were no discernible effects. Since the cloud chamber techniques utilized in this study are sensitive to extremely subtle physical effects, the absence of any visible indications is strong evidence of null effects.

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* The electric fields required are at least 10^8 volts/cm, and can be attained with our equipment by Q-switching the laser and focusing the resulting beam to a point. A net volume of 1 to 2 mm^3 about the focal point of the lens is thus exposed to these intensities.

2.2 Observations in Absorbing Media (Resonant Laser Effects)

With the addition of absorbing media, the physical effects observed were enhanced, with a resulting reduction in the threshold required for discernable effects by several orders of magnitude (this explains effects such as illustrated in QPR No. 1, page 8 and QPR No. 2, page 11). At such reduced intensities, given laser equipment can cover a much larger volume, as focusing is not required. Without Q-switching, overall efficiency is further increased. The mechanism involved is believed to be based on local heating of the absorbing material, a well-known effect of laser irradiation.

2.3 Conclusions on Aerosol Fogs

The direct physical effects of laser irradiation on non-absorbing media are feeble unless very high electric field strengths ($\sim 10^8$volts/cm) can be attained over a large volume. This has only recently become possible.(4) This is the case applicable to ruby (or Nd) laser irradiation of DMMP.

Absorption clearly enhances the observed effects, implying that "seeding" with absorbing materials can have great value when ruby or Nd lasers are necessary. The other possibility is the use of the newly available CO_2 laser, which is expected to deliver energy quite efficiently to DMMP (but not to surrounding air or water vapor) over relatively large volumes.

Desirable experiments that would relate to potential applications are:

(1) Finding suitable seeding substances for use with aerosol fogs and ruby (or Nd) lasers.

(2) Study of CO_2 laser effects on aerosol fogs as a function of available laser operating conditions.

(3) Keeping in mind that H_2O vapor could be a practical seeding substance, look for laser sources resonant with H_2O,and study their effects on H_2O fogs, especially their ability to co-condense and occlude small quantities of non-absorbing atmospheric contaminants.

(4) High energy effects other than direct conversion of laser light to thermal form have some potential value for aerosol fog condensation. For example, an acoustic shock wave is known to be produced by laser breakdown, and has been well characterized.(5) High energy pulsed laser equipment is necessary, but the results may be faborable compared to presently known acoustic methods of aerosol fog removal.

(5) Given the decomposition products of laser irradiation of DMMP (covered in Section 4.0), methods should be considered for chemical means of benefiting from these products.

3.0 AIR ACTIVATION (Item II)

With the stated contract objective in mind, we have performed a number of experiments relevant to chemical activation of various mixtures of air, water, DMMP, and normally present impurities.

3.1 Optical Spectra

We have looked for optical spectra of the laser breakdown spark both in absorption and in emission, visually as well as with crude grating instruments and wedge filter instruments. Visual results indicate no detectable effects whatever below breakdown intensities. Emission spectra such as taken by crude grating techniques[1] appear to show only a simple continum spectra characteristic of a very high temperature black body. Somewhat better techniques were attempted with a wedge filter spectrometer[6] with no significant advantages of the slightly higher resolution. These observations apply to the DMMP in vapor form as well as in liquid form.

We conclude that more detailed study of optical emission spectra is not warranted in the absence of indications of any line type spectra. The fact that breakdown in the liquid occurs at a sufficiently low threshold level as to preclude the stimulated Raman effect (observations of which were originally attempted) prevents us from observing the stimulated Raman spectrum, which would otherwise be of great value. The very high brillance of the breakdown spark, and the absence of any visible indications whatever at lower laser intensities, shows optical absorption spectroscopy to be of no potential value in this work.

3.2 Pulsed NMR

The observation of highly intense breakdown sparks during laser induced dielectric breakdown in liquid DMMP heightened our expectation that free radicals, among other chemically active species, would be observed on our proposed pulsed NMR experiment. The simplest available techniques were used, geared specifically to the problem of finding free radicals, and the appropriate measurements in NMR were carried out simultaneously with irradiation of the sample with a laser beam focused to breakdown intensities.[7] Several repetitions of this experiment showed no effect that could be attributed to the laser beam. This experiment was fully analysed for its experimental implications.[8]

Though a null effect was observed with a focused, Q-switched laser beam acting on DMMP, the technique remains perfectly applicable to cases where the entire sample volume is irradiated at full electric field intensity. Suitable circumstances under which this experiment should be repeated are forseeable, in terms of the chemical analysis of stable products to be discussed in Section 3.4.

3.3 EPR

Since the required equipment was already available, the basic experiment on detection of free radicals by electron paramagnetic resonance was attempted.(9,10) At a very early stage, indications were seen that the lossiness of DMMP at the available operating frequency would cause serious problems. After a very brief attempt to circumvent these problems, further effort along these lines was terminated. The principle involved in the proposed experiments is still applicable, however, and further effort, possibly at different operating frequencies, would be warranted in the event of positive results with the NMR experiment of Section 3.2. The additional value of this experiment would be more specific identification of the free radicals concerned.

3.4 Chemical Analysis of Products

The results of the above experiment, plus our preliminary chemical analysis, showed that irradiation of DMMP results in decomposition product levels of less than 1 part per million. Variations in impurities, water vapor, or air mixed with the samples did not change this conclusion. In large part this is a "geometrical" problem rather than a yield problem, because the high electric fields required to produce observable effects with our equipment can be made to cover a volume the order of 1 mm^3, whereas, practical sample tubes utilized must be larger than 1 cc, or breakage occurs under laser irradiation. Thus the actual chemical yield is reduced by at least three orders of magnitude with presently available laboratory techniques, which makes analysis difficult, but requires extrapolation to conditions that may be visualized with newly available equipment capable of covering much larger volumes with the required high intensities.(11) (Note: We stand in strong disagreement with the conclusions expressed in Reference 11. Our actual experience with DMMP substantially deviates from the author's ideas. We require much higher electric fields than suggested in this article to observe even the most subtle effects.

The two techniques available for analysis of stable products of laser irradiation are vapor phase chromatography and mass spectrometry. With flame ionization detectors,(12) chromatography by far exceeds the sensitivity of mass spectrometry, however, characterization of a product by its retention time does not identify it. An extrapolation technique which is considered valid, applies when a characteristic retention

time has been observed by chromatography at high levels of concentration, as well as at marginal ones. Mass spectrometric analysis coupled with chromatography of the stronger sample will yield identifications applicable to the weaker sample. Analyses of parts per million are quite feasible by these means.

Our observations to date have relied primarily on chromatography with some initial results on a time of flight spectrometer. Further work remains to be done to identify the characteristic products observed to date, but impurity problems initially encountered in the DMMP have been basically solved. (Careful discussions with Mr. Hites, who ran the original chromatograms at MIT with the mass spectrometer, showed that he was in fact observing only DMMP and its phosphite impurity, specifically dimethyl phosphite, $(CH_3O)_2PH$) .

3.5 CO_2 Laser

Though practical devices of this type were unknown and unavailable at the start of our contract work, we have kept abreast of its potentialities for Infrared resonance effects with DMMP and related materials. As soon as we became aware of this technology in sufficient detail, we pointed out its practicality and value and began construction of equipment(13) flexible enough to satisfy the objectives of this contract.

This CO_2 laser equipment produces several watts in the neighborhood of 10.6 microns as discussed in detail in our progress reports.(14)

The principle interest in this laser lies in the fact that since its output is strongly absorbed by DMMP and not by air constituents or water vapor, it provides a selective means of coupling energy to DMMP, or other suitable materials. The efficiency with which this energy can be produced along with the fact that it is absorbed even at low electric field strengths, can materially ease the yield problem characteristic of the ruby laser which requires extremes of intensity to produce discernible effects. Since it is possible to Q-switch as well as tune the CO_2 laser, it should be feasible to explore the possibility of quantum effects at higher intensities in addition to the significant thermal decomposition observed at low, but constant power, with the normal mixture of frequencies.

3.6 Conclusions on Air Activation

After exploring a wide variety of techniques that appeared promising a priori, we have found the chemical analysis techniques discussed in Section 3.4 to be the ones of major value in the present state of our laser technology. The yield problem mentioned there makes the application of these techniques difficult as well. At the present stage the basic tech-

niques have been established and actual time expended in running specific analyses can be much reduced. These techniques have been of great value in evaluating our experiments both with the ruby and the CO_2 laser.

4.0 LASER INDUCED DECOMPOSITION (Item I)

Originally the resonant decomposition studies in the infrared were made optional for lack of suitably intense sources to accomplish the desired objectives. The advent of the CO_2 laser makes studies of decomposition of DMMP much more practical. Though much of this work fits in with the objectives of Section 3.0, the aspects of interest for decomposition as opposed to air activation are repeated here with a somewhat different emphasis. Figure 1 provides a schematic comparison of the phenomena discussed in this section.

4.1 CO_2 Laser

In addition to scanning the literature on this subject, we have kept well informed of the current technology through personal contacts with individuals working in this field. As a result, we have produced a simple CO_2 laser that is capable of basic laboratory studies in this field. The principle features that are not available in commercial equipment are the possibility of Q-switching, which will be needed ultimately to distinguish thermal from optical pumping types of effects, and the possibility of tuning the output to specific values of the many available laser frequencies.[13, 14]

4.2 Relation to Section 3.0

The principle relation of these measurements to that of Section 3.0 lies in the fact that the same types of chemical analysis will be applicable to both air activation (or activation of other constituents) and to decomposition effects. This is because the transient products of activation have not appeared in sufficient quantities to be observable by any techniques other than analysis of chemical end products. Chromatography is most sensitive and capable of indicating the presence (or absence) of various products. Positive identification of the products is only possible through mass spectroscopy, which presently requires several orders of magnitude more than chromatography. In any event, products detected by chromatography can be characterized by their retention times.

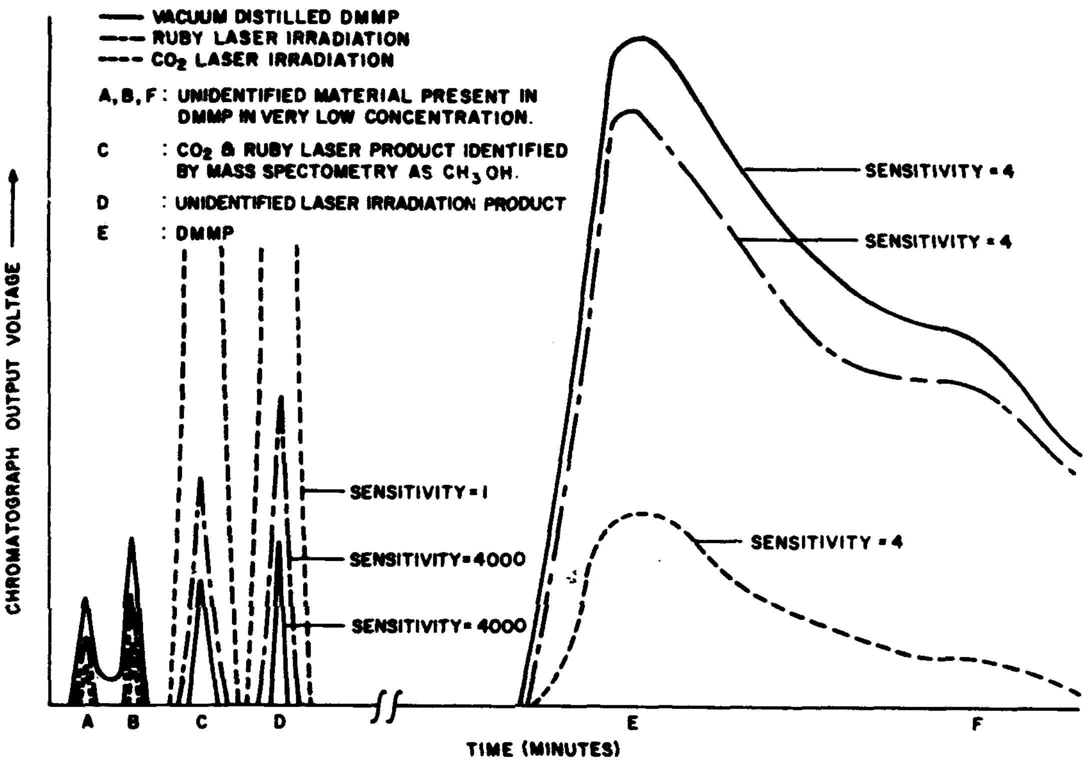

Figure 1. Schematic Illustration of Chromatograms of DMMP Exposed to Laser Irradiation.

4.3 Conclusions on Laser Induced Decomposition

Up to the present date experiments have been performed and the following conclusions are available.

(1) The CO_2 laser has been completed and irradiations have been performed on a number of samples of purified DMMP, in some case with impurities such as water added. The only decomposition products observed were identified as products C* and D+, which are also the products found to result from thermal decomposition of DMMP. These experiments are all described in further detail in Progress Report No. 6. A quantitative feature worth noting was that a 2 minute exposure of about 2 cc of DMMP to several watts of power at 10.6 m microns produced the order of 11% decomposition of DMMP. This can have great practical significance in decomposition of aerosol fogs containing DMMP, especially if pulsed operation favors decomposition over evaporation of the droplets.

(2) The above described effects relate to irradiation of DMMP liquid. Experiments on the vapor were inconclusive because of a severe problem with catalytic decomposition of DMMP on the metals present in the ampule crusher and injector of the gas chromatograph. The experiment and the problems associated with it are described more fully in Progress Report No. 7.

During those experiments it was noted, however, that the absorption in 10 cm of vapor at the room temperature vapor pressure of DMMP was quite feeble. This implies that decomposition was rather unlikely at the laser intensity levels used, because a significant rise in temperature requires a commensurate dissipation of power per unit volume according to the equation:

$$\frac{\Delta P}{\Delta V} = -\alpha I$$

where:

$\frac{\Delta P}{\Delta V}$ = power dissipated/unit volume,

I = intensity (Watts/cm^2),

α = absorption coefficient (cm^{-1}).

* Product C has been positively identified as CH_3OH, methyl alcohol, by its characteristic patterns in mass spectroscopy.

\+ Product D has not been identified because no corresponding mass spectrum appeared. The possibility of secondary reactions with O_2 or H_2O could further complicate the analysis. At presently available concentrations, the analysis is feasible, but will require a significant effort.

Clearly, high local power dissipation is favored by high beam intensities. The maximum intensity available from a collimated CO_2 laser beam is limited. If this level, in an optimally designed laser, proves inadequate, then decomposition of vapor would require a focused beam. Focussing the beam increases available intensities, but at the sacrifice of volume in which the beam is at full intensity (similar to the problem encountered with ruby lasers).

(3) Ruby laser irradiation, when focused to intensities to produce dielectric breakdown, has been found to yield the same thermal decomposition products discussed above. Because of the yield problem associated with the required focussing of the beam, the amount of these products produced were just barely detectable. Under MITHRAS' company sponsorship the search is being continued with higher laser intensities and with the most sensitive possible chromatographic techniques for possible products of ruby laser irradiation with larger molecular weights than DMMP. This search was suggested by some other MITHRAS supported work on azo compounds in which an unexpected product, of high molecular weight, was discovered which was distinctly not the expected product of a simple two-photon process. This work is discussed in some detail in Appendix C of QPR No. 7. It is expected that either the multiphoton effects or the soft X-ray effects associated with laser induced dielectric breakdown can produce unique molecular rearrangements not attainable by simple heating. (Some of these possibilities were discussed in QPR No. 5, Section 2.1.)

(4) It is quite conceivable that simultaneous irradiation at, say ruby and CO_2 laser frequencies together, could produce unique effects. At least, it should be possible with CO_2 irradiation to reduce the threshold for breakdown at the ruby laser frequency. It was not judged appropriate to carry out such experiments in view of the considerable amount of effort still required for complete quantitative studies of the effects of these two lasers individually.

5.0 ASSOCIATED TECHNIQUES

As called for by the nature of this work, we have developed a number of techniques of observation that initially appeared promising for observation of transient and permanent effects of laser irradiation. As might be anticipated, some of these methods produced negative results, at the available levels of sensitivity, while other techniques proved to be the methods of choice in this study. All the significant techniques attempted are discussed below.

5.1 NMR Analysis

The steady-state NMR analysis played a role in characterization of the bonds in DMMP. This work was completed and published.[15] Future applications of these techniques are conceivable to characterize end products, but at presently available concentrations, further studies of this nature are not warranted.

5.2 Infrared Spectroscopy

Infrared spectroscopy was considered, but judged unsuitable at the product concentrations involved. Concentration of sufficient end products by repeated ruby laser firings is entirely prohibitive in view of laser technology.

5.3 Cloud Chamber Techniques

Cloud chamber techniques, in several forms were an original development of the work on this contract. Some special aspects of current scientific interest has lead to publications.[2,3,15] Cloud chambers have been used to produce some conditions of interest; further, to observe some of the presently feeble effects which might well prove to be important as high energy ruby and neodymium laser technology makes it possible to cover large volumes at the desired light intensities.

5.4 Pulsed NMR Techniques

Pulsed NMR techniques were developed in an especially simple form suitable for detection of free radical effects. Though the concentrations observed to date were below the sensitivity threshold of this technique, applications are still foreseen when lasers that cover larger volumes at suitable intensities become available.

5.5 EPR

Electron paramagnetic resonance techniques were on hand and required little adaptation for preliminary trials of free radical detection capabilities. As soon as the first attempts were made, it was realized that the available operating frequency was not suitable for work with DMMP. The basic idea is still applicable, but equipment of a lower operating frequency would be necessary to carry them out, and the expense would be justifiable only if other indications revealed sufficient production of free radicals to make their characterization with this instrument certain.

5.6 Optical Spectroscopy

Optical spectroscopy was considered, and simple applications of diffraction gratings and wedge filters were carried to the point where the spectra were shown to lack line structure that might provide information of any value toward our objectives. Under circumstances where a highly colored breakdown discharge appears, it would be advisable to repeat such experiments, and carry them further if discrete spectra were observed. Since we saw what appeared to be continum radiation characteristic of extremely high temperatures, and all results to date have been consistent with this supposition, no further studies of optical spectra were attempted.

5.7 Laser Technology

The laser technology required was carried by us to the state of the art as judged to have bearing on this study. In addition to the many improvements and procedures that had to be developed, even when starting with commercially available ruby laser equipment, we have found the applicability of the new CO_2 laser techniques and carried out the design and construction of an instrument of value in these studies.

5.8 Purification of DMMP

Because initial experiments showed that the material received from the manufacturer had a few percent of dimethylphosphite as an impurity, conclusive experiments required purer material. Several methods of purification were attempted, and it was found that extreme care was necessary to prevent detectable decomposition due to simple thermal effects, and in some cases to catalytic decomposition when metals were exposed to the DMMP vapor. The final method adopted was vacuum distillation at the lowest possible temperatures and at vapor pressures of about 3 mm Hg. Progress Report No. 7 includes some details of the distillation procedure in Section 2.2.1.

5.9 Chemical Analysis Methods

Vapor phase chromatography with heated columns was an applicable technique when the correct packing was used. Because of the catalytic decomposition found to take place in the presence of metals, only a glass column could be used. Both helium and nitrogen have been used on different occasions as the carrier gas. A flame ionization detector has been found essential to obtain the sensitivities required. Section 2.2.2 of QPR No. 7 provides some typical operating conditions.

In order to identify products in addition to their characterization by retention times, mass spectroscopy was found a valuable technique. The resources of Prof. K. Biemann of the MIT Chemistry Department were of great help in several trial experiments. A Bendix time-of-flight spectrometer was used, and had to be preceded by a chromatograph in order to identify and resolve the feeble decomposition products of laser irradiation. Unfortunately the three orders of magnitude weaker sensitivity of this instrument as compared to the flame ionization detector makes it difficult to identify some conceivable decomposition products. Preparative chromatography would be necessary in such cases to concentrate the product to a detectable level.

6.0 GENERAL CONCLUSIONS

6.1 Physical Effects

(1) The physical effects of ruby laser irradiation on DMMP are in general quite inefficient. This is to be expected since no absorption takes place in this part of the spectrum at normal intensities. As intensities are increased beyond the threshold for laser induced dielectric breakdown (10^8 volts/cm), physical and chemical effects are observed. The first effect to appear is heating due to the high local absorption of energy during the breakdown process. Next to appear are chemical effects, starting with the decomposition products to be expected from heating. At still higher intensities, somewhat more complex physical and consequently chemical processes are expected to occur, but have not been conclusively demonstrated with DMMP at the laser intensities available to date. Though these laser effects are of potentially great fundamental value, due to their uniqueness, immediate applications to decontamination and protection are not foreseen because the intensities required to achieve any measurable effect only can be achieved over extremely small volumes, with poor efficiency. The unique effects to be anticipated involve selective formation of free radicals, radical-radical reactions, and other kinetic phenomena unaccompanied by competing processes that might predominate in a high temperature reaction.

(2) Some attention was given to the possibilities of physical nucleation of vapor fogs with ruby lasers. Our cloud chamber studies have shown that indeed physical nucleation is possible, but takes place under exceptionally delicate conditions, and at laser intensities that can be achieved only over very small volumes. In addition, the focusing required to produce these effects would be marred by excessively dense fogs. Physical condensation of aerosol vapor fogs is, therefore, judged to be impractical under "open-air" conditions. Controlled environments within enclosed chambers, on the other hand, offer some practical possibilities that appear worthy of further consideration, to the extent that laser irradiation has been found to influence (and accelerate) condensation in the cloud chamber environment. Conceivably, filter devices could be based on circulation of air through irradiated chambers.

(3) The vapor of DMMP does not appear strongly affected at normal CO_2 laser intensities. In principle, the same effects are obtainable as with the liquid, at sufficiently high intensities. The state of CO_2 laser technology will determine the practicality of decomposing DMMP vapor by CO_2 laser irradiation.

(4) The CO_2 laser produces significant heating effects in liquid DMMP, presumably also in the aerosol. The reasonable yield and the convenience in delivery of energy to a relatively large volume suggests a potential value in practical applications. Further studies of effects of CO_2 irradiation on aerosols are deemed advisable.

6.2 Chemical Effects

(1) Chemical effects of laser irradiation follow closely the occurrence of physical effects. Ruby laser irradiation causes no observable decomposition below intensities of the order of 10^8 volts/cm. Above these intensity levels, dielectric breakdown takes place and laser energy is absorbed. The threshold level of breakdown correlates with the appearance of the thermal decomposition products of DMMP and C* and D+. It appears very likely that at higher intensity levels other physical processes than simple heating will be significant, and corresponding, unique, chemical products will be formed. Either multiphoton processes or soft X-rays (both of which have been associated with laser induced breakdown) can be responsible for these processes, in characteristically different ways.

(2) With CO_2 laser irradiation, where multiple photon reactions are much less likely to yield quantum energies in the photochemical range, only thermal decomposition products are to be expected. The yield of these thermal products, with readily achievable laser irradiation conditions, is significant. Though the products are not unique, the convenience of delivering thermal energy offered by the CO_2 laser could well be a basis for practical applications.

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* Product C has been positively identified at CH_3OH, methyl alcohol, by its characteristic patterns in mass spectroscopy.

\+ Product D has not been identified because no corresponding mass spectrum appeared. The possibility of secondary reactions with O_2 or H_2O could further complicate the analysis. At presently available concentrations, the analysis is feasible, but will require a significant effort.

(3) Other laser sources exist today than were foreseen when this work was begun. The neodymium glass laser is expected to yield results that are similar in general to ruby irradiation since DMMP is transparent to 1.06 microns as well as to .6943 microns. The conditions for dielectric breakdown may differ, but above the threshold, identical thermal decomposition products are expected. Because of the different photon energies, one would expect differences in the photochemical products, if any, produced at still higher intensities, but this is still a matter of speculation. In terms of practicality, and economy in covering a maximum volume at high peak intensity levels, neodymium laser sources might be preferred over ruby.

(4) Several laser sources have been discovered that produce intense ultraviolet radiation. Chemical decomposition effects are expected to show high quantum yields, at least for sources of the right frequencies, by the very relation of these photon energies to the processes studied in the conventional photochemistry. Harmonics (second and third) of ruby lasers, which can be generated at laser intensities, are comparable to direct laser sources in the ultraviolet.

(5) Efficient far infrared lasers are becoming commercially available, such as those utilizing water vapor, nitrous oxide, and cyanide. Though some of these sources may ultimately offer many of the practical advantages of the CO_2 laser, it appears that their operating frequencies are not as well suited to transmission in the atmosphere (and through water vapor) as the CO_2 laser.

7.0 RECOMMENDATIONS FOR FUTURE WORK

Based on our experience to date, our recommendations for further work on the effects of laser irradiation on DMMP and related materials lean toward studies more directly related to the practical aspects of this program.

(1) Much more intense ruby/or neodymium lasers should be used (somewhat over 1 joule, Q-switched) to better characterize the photochemical products associated with laser induced dielectric breakdown phenomena. Because of the unique nature of the decomposition reactions to be expected, this area merits further study.

(2) The use of simple CO_2 lasers on aerosol fogs appears quite practical, and further studies should be done aimed directly at furthering the potential applications.

(3) Detailed studies of chemical yield versus laser operating conditions, as well as presence of H_2O, or other contaminants, appear advisable in general. Because of the immense variety of conditions and systems so far encountered, this work can best be done in the required amount of detail if a suitable selection is made of the two or three systems and sets of conditions of maximum present interest.

(4) Chemical analysis by chromatography is the technique of choice for most laser irradiation studies. Much more profuse and accurate data is to be expected if the chromatograph and laser equipment are operated simultaneously in the same laboratory. The analysis would be rapid, and the prospects improved for detecting less stable products and for avoiding undesirable effects such as catalytic decomposition in associated containers.

(5) Ultraviolet laser irradiation appears desirable, at least for basic studies. Atmospheric transmission will certainly not present any problems in the absorption region of DMMP which occurs around 260 mμ.[16]

(6) Physical nucleation of aerosol fogs does not occur without saturation conditions. In an enclosed chamber, with thermally controlled surfaces, practical possibilities exist. The occlusion of noxious vapors in a medium such as H_2O, whose precipitation can be influenced by a resonant laser source, is a possibility deemed to merit further consideration.

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13. ABSTRACT A research program on laser irradiation effects on DMMP is reviewed. Physical and chemical effects of exposure to 0.6943μ radiation from ruby lasers and 10.6μ radiation from a CO_2 laser were studied by a wide variety of laboratory techniques. Comparisons and conclusions relate to the practicability of laser irradiation for decontamination and protection purposes. Ruby laser effects of vapor fog nucleation are not observable without extremely high intensities, and even then, physical condensation requires very carefully controlled laboratory conditions. Ruby lasers produce very little chemical decomposition, at the power levels available in this study, and require intensities at least sufficient to produce dielectric breakdown at the laser frequency. The CO_2 laser produces chemical decomposition products do not differ from simple heating effects, but are of sufficient magnitude to justify further laboratory studies.

14. Keywords

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